Optimization of PEEM-2 for studies of organic thin films

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INTRODUCTION

There are many potential applications of X-ray photoelectron emission microscopy (X-PEEM) to organic thin films, such as fundamental studies of phase separation [1], and applied studies of organic light emitting diodes, adhesion promoters [2] etc. In order to obtain meaningful results, it is important to understand the challenges of applying X-PEEM to organics, and to develop compensating data acquisition strategies. These challenges include: radiation damage, camera artifacts, Io determination, higher order radiation, charging, sample damage from field emission or discharges.

The photon flux at BL 7.3.1 ($>10^{12}$ photons/s at 500 eV in a 30x300 μm spot, with 1.9 GeV, 400 mA) is very high because there are only two optical elements and energy resolution is sacrificed for flux. The high flux, combined with a relatively inefficient electrostatic column (~5 % transmission at high spatial resolution – 12 μm aperture) and an inefficient camera, mean that ratio of detected signal to number of photons absorbed in the near surface region is very small. In order to perform useful chemical analysis, images of the region of interest must be recorded at a number of energies (in the C1s, N1s or O1s regions for organic samples) to form an image sequence which can be subsequently analysed to obtain point or region spectra, or chemical maps. Other problems occur because of limitations of the CCD camera - bad pixels; pixel-to-pixel variation in dark signal (leakage) and gain; as well as a slow data transfer rate (0.25s/image, no ability to transfer sub images). A further challenge is the uneven illumination in the PEEM; in order to gain sensitivity we use reduced magnification. Typically the camera views 60x60 μm^2 but only the central third of the image is illuminated.

In order to reduce the damage rate we work at much reduced flux, achieved by placing an aperture (formed by two independently adjustable elements, called 'chopper' and 'mask') in the beam before the monochromator. This reduces the energy resolution as well as the flux – at a chopper value of 15 the resolving power is only 100. Under typical low dose conditions we work with less than 10% of the dynamic range of the camera. Background and camera corrections are extremely challenging. It is essential to record Io spectra from a suitable reference surface, typically HF-etched silicon for organic thin film samples deposited on Si or Si_3N_4. This is especially true in the C 1s region where there is a lot of structure in the Io spectrum. The Io signal must be measured under very similar conditions to those used to study the sample in order to ensure the same sensitivity, energy resolution and higher order content, (the latter two depend on the exact choice of chopper, windows, slits and filters used). The PEEM sensitivity is very dependent on the sample-objective lens distance, which changes every time a sample is re-positioned.

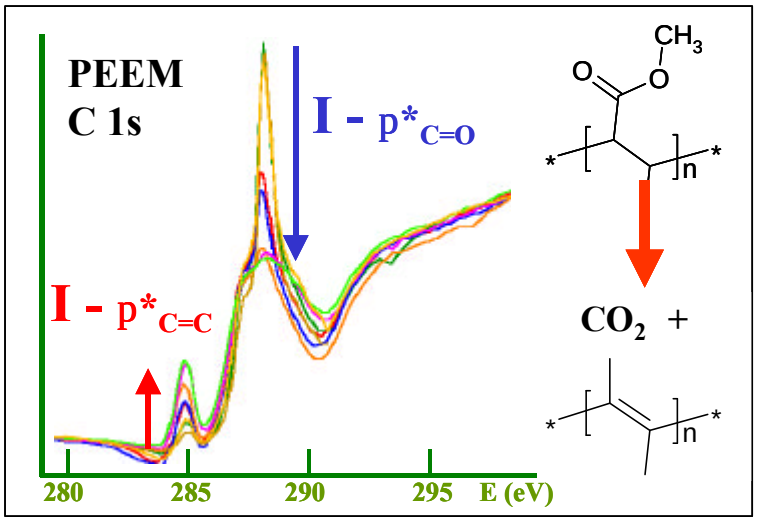

Fig. 1 Plots of C 1s NEXAFS of a 50 nm PMMA film on c-Si. Successive scans made on the same spot build up dose and damage.

Charging can occur for any insulating sample, although it is often surprising the samples that can be studied by PEEM. We typically observe charging if a polymer sample is too thick (> 75 nm), or too corrugated (> 15 nm rms). In some cases a thin metal coating (<2-3 nm) can be evaporated to control charging. Charging results in dark spots on images, where the electrons are trapped by the surface charge potential, or in bright spots, where there is artificially enhanced emission by discharges or, at locations of high curvature, by enhanced detection

probability due to stronger fields. While it is sometimes possible to record meaningful NEXAFS spectra from charging surfaces, more typically, charging results in large and variable sample or objective lens currents which lead to unstable operation, and, in extreme cases, macroscopic discharges that can damage samples, making dramatic dendritic patterns in organic layers, and exploding Si_3N_4 windows. In the following we describe a systematic study of a pure polymethylmethacrylate (PMMA) film in order to characterize its radiation damage rate, and thereby develop procedures to study heterogeneous samples containing PMMA in a meaningful fashion, despite these challenges. A detailed manual for operating X-PEEM and choosing parameters optimal for radiation sensitive samples is available at the beam line or from the authors [3].

EXPERIMENTAL

~50 µl of a 1.0% w/w toluene solution of PMMA (Mw = 112.3 K, Mw/Mn = 1.09, Polymer Source Inc) was passed through a teflon filter to remove particulate impurities and dropped onto a spinning HF-etched Si chip at 4000 rpm. Spinning was continued for ~5 s. The film thickness was estimated to be ~40 nm from AFM at a scratch and the rms roughness was 6 nm The sample was not annealed.

Property	Value	Property	Value
Mask	0.9	Dwell (s)	3
Chopper	15 or 16	Camera gain	normal, x8
Al window #1	in	PEEM aperture (µm)	50
Al window #2	in	Sample (kV)	18.0
Exit slit	in	Objective (kV)	13.68
Ti filter (150 nm)	in	Transfer (kV)	12.45
Flash light	on	Intermediate	13.78
Background (Hz)	50	Projection	0

The relationship of measured intensity to the various parameters controlling the signal is summarized in **equation 1**. A number of scale factors need to be determined but this qualitative formula may be useful for others using PEEM-2 for organic thin film studies.

$$S = G*t*[I*\sigma*f_{esc}*F*\varepsilon_{PEEM} - B] \quad \text{(eqn 1a)}$$

where S = detected signal , G = camera gain (2,4,8), t = time, σ = cross-section, f_{esc} = electron escape probability (integrated over inelastic scattering and angular effects), F = work function, ε_{PEEM} = PEEM column efficiency [α (magnification)* (aperture)^2], B = no-X-ray background, and I is the flux (ph/s) on the sample, given by

$$I \alpha\ I_{ring}*C*T \quad \text{(eqn 1b)}$$

where C, the chopper factor is $(C_{max}-C)/C_{max}$; and T, the Ti filter factor, is $(T_{max}-T)/T_{max}$.

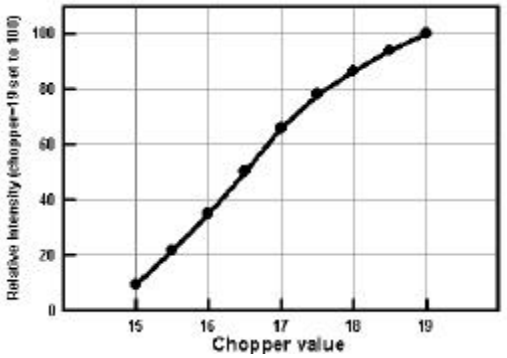

Fig. 2 Variation of flux on sample vs. chopper.

RESULTS AND DISCUSSION

Fig. 1 shows a typical sequence of spectra (without Io correction) recorded while the sample was being damaged. The relative radiation damage rate for PMMA in the low dose regime was determined by recording successive image sequences on the same spot, using the instrumental parameters listed in table 1. Only 24 energies in 283-295 eV range were used in order to track damage changes adequately. In general keeping the number of sampled energies to the minimum is a key step in making meaningful measurements of organics. The *relative dose* was obtained from the integrated spectral signal up to a given measurement, taking into account the dead time between images (~2 s). The *relative damage* was obtained from the increase in the area of the 285 eV $\pi^*_{C=C}$ peak (growth of reduced sites in the backbone) and decrease in the area of the 288 eV $\pi^*_{C=O}$ peak (loss of acrylate groups). In addition to the measurements made at low dose, another series at much higher dose (5 or 10 s exposure at chopper 19) was performed. The two sets were matched in the overlapping region of the 285 eV and 288 eV damage curves. Finally the dose scale was expressed in terms of time equivalent at full flux in the carbon 1s region using the variation of signal strength with chopper setting to scale the times (**Fig. 2**).

Fig. 3 plots damage versus relative dose for PMMA as measured in the PEEM As is typical in radiation damage curves, there is an exponential change with saturation. Based on these results, we estimate that, at the full flux dose rate (chopper = 19, 400 mA in the ALS), the total acceptable exposure time for meaningful measurements of samples containing PMMA with negligible damage (as measured by spectral change) is 10 seconds. Since it takes about 5 seconds to record an image of acceptable quality, if full flux is used it is only possible to record a few images before the PMMA in a PMMA-containing sample is irreversibly modified. We note that a recent study of radiation damage in various polymers by STXM [4] indicates that PMMA is about average in terms of radiation sensitivity.

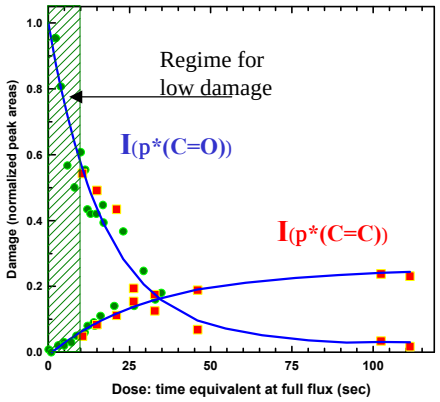

Fig. 3 Intensity at 288 eV and 285 eV versus accumulated radiation dose. The dose is time to equivalent deposited energy when PEEM is operated with full flux. The green points are measurements made at reduced flux. Chopper: green (15), red (19).

Chemical imaging with PEEM requires images at a number of energies.Typically 10-15 images are needed. The only way to get these without "frying the sample" is to "turn down the torch". We routinely do this by using the chopper to reduce the flux ~10-fold (see Fig. 2). This allows 10-20 images to be recorded prior to significant damage. Chopper values below 15 are not useable since the grating is inadequately illuminated. 2-bunch mode is also useful, but normalizing the rapid time variation of flux is a challenge.

Fig. 4 presents results of a low dose study of a 20:80 (w/w) PS:PMMA film (PS = polystyrene) which has domain sizes on the order of 250 nm as determined by prior AFM measurements. This is a continuation of our earlier studies of phase segregation on PS:PMMA blends [1]. We are trying to develop a metastable system with flat, reasonably large domains that are pure PS and PMMA, in order to carry out competitive protein adsorption studies. As the analysis of the spectrum of the PMMA-rich regions shows, the as-made material still contains significant PS, as found earlier [1]. However, with our refined understanding of the damage rate of PMMA in PEEM-2, we are now very confident that the 285 eV signal observed in the PMMA-rich domains is from incompletely phase segregated PS and NOT from the C=C bonds formed from radiation damage of PMMA (Fig 1).

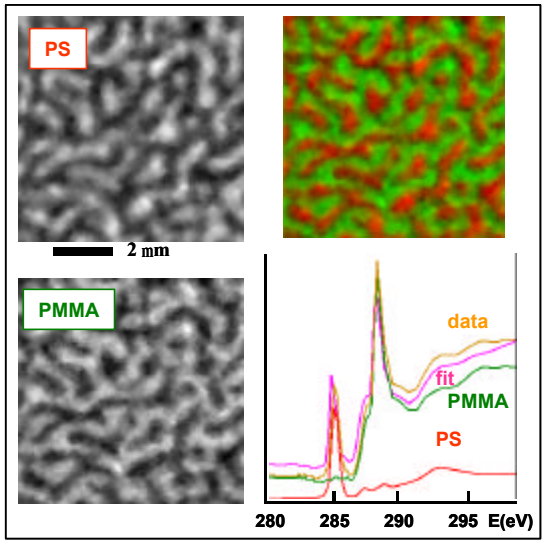

Fig. 4 PS and PMMA component maps, and color composite derived from image sequence of as-made 20:80 PS:PMMA blend, using low dose protocol (3s dwell, chopper=16, few points). Lower right shows the results of a curve fit to the spectrum of pixels in strong PMMA regions. (Jun-01).

SUMMARY: Relative dose - damage relationships for PMMA were measured in PEEM-2 to define an acceptable regime [5]. Similar calibration measurements are required prior to study of other radiation sensitive samples. Self-assembled monolayer and micro-contact printed systems involving fluorocarbons are particularly challenging due to their very small thickness (< 5nm) and extreme radiation sensitivity. An even more rigorous application of the methods outlined in this report is required for successful studies of such materials.

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3. C. Morin, A.P. Hitchcock, H. Ikeura-Sekiguchi, A. Doran and A. Scholl, PEEM-2 manual (2001).
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5. C. Morin, A.P. Hitchcock, et al in preparation.

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